# Aggregation-induced emission and temperature-dependent luminescence of potassium perylenetetracarboxylate

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## Abstract

Investigation of temperature-dependent photoluminescent properties of potassium perylene-3,4,9,10-tetracarboxylate ($K_4PTC$), a molecule with no internal rotational degrees of freedom, shows aggregation-induced enhanced emission at room temperature. The different excitonic emission processes are dependent of temperature, some of which quenches in an intermediate temperature range (from 50 to 150 K). The exciton excited states switching phenomenon from "dark" to "bright" states is observed and its explained using Herzberg-Teller selection rule. $K_4PTC$ is a molecule comparable to the size of its precursor, perylene-3,4,9,10-tetracarboxylic anhydride (PTCDA) and is highly soluble in water, contrary to PTCDA, which is poorly soluble in most solvents. Powder x-ray diffraction measurements corroborate a lesser degree of ordering of bulk $K_4PTC$ compared to bulk PTCDA. The green luminescent molecule could, in principle, be used as a biomarker, or in photodynamic therapy, if further studies show relatively low toxicity.

Keywords: PTCDA, $K_4PTC$, aggregation induced emission, temperature dependence.

## 1. Introduction

The metallic complexes and salts of perylene-3,4,9,10-tetracarboxylic anhydride (PTCDA) are promising candidates to different technologies, from photovoltaic devices, [1] dyes, including biochemical analysis, [2] to OLED displays [3] and quantum devices.[4] Recently, a three-dimensional metallorganic framework (MOF) was synthesized using perylene-3,4,9,10-tetracarboxylic acid (PTCA) and KOH.[5] This MOF showed to be potentially useful to build humidity actuators on flexible substrates with printed techniques.[5]

In our previous work, a new terbium complex, $Tb(H_3PTC)_3$[H4PTC = perylene-3,4,9,10-tetracarboxylic acid], or $Tb(H_3PTC)_3$ , was synthesized and its luminescent properties were investigated.[3] Among its remarkable properties, a bright luminescence was observed, which was measured in films and bulk, by using several optical techniques.[3] Here, we present the optical properties of potassium perylene-3,4,9,10-tetracarboxylate ($K_4PTC$). $K_4PTC$ has been investigated as an electrode for

batteries.[6,7] However, little is known about its optical properties, specially regarding its photoluminescence.

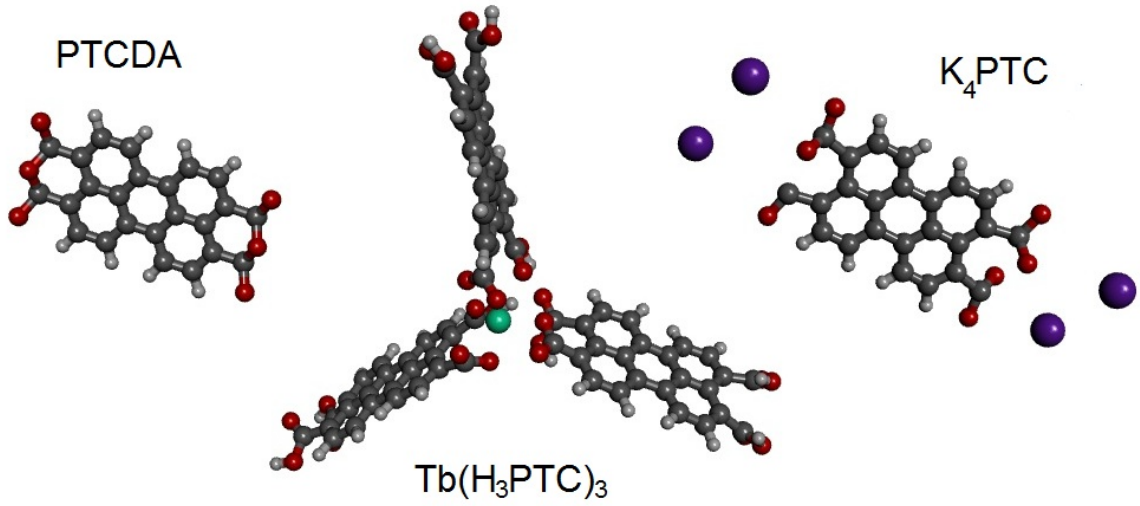


Fig. 1. Chemical structure of PTCDA, $Tb(H_3PTC)_3$ and $K_4PTC$. Dark grey, light grey and red atoms in the PTCDA molecule represent C, H and O atoms, respectively. The green atom in the center of the $Tb(H_3PTC)_3$ structure represents a Tb atom. Blue spheres in the $K_4PTC$ represent K atoms.

When treated collectively, molecular electronic excitations generated through absorption of light quanta are better described as excitons, a pair of electron and its counterpart, the hole, an empty electron state in the valence band, in a molecular crystal. If the electron and the hole are bound to each other, with an energy below 1 eV, it is said that they form a Frenkel exciton. As in an atom, an exciton can show quantization in energy, with discrete values that range from its fundamental state to the free exciton state, when the electron is separated from the hole. Therefore, above the energy of the exciton fundamental state, there are excited exciton states, which in low temperature are generally empty, since excitons rapidly thermalize to the fundamental state. After reaching fundamental state, an exciton can be eventually annihilated, through generation of a photon, creating fluorescence or phosphorescence. However, when temperature rises, the vibrational quanta (phonons) of the system increases and generates two effects that can interfere with exciton annihilation, even by diminishing photon emission through phonon scattering or by modifying the selection rules (caused by vibrations that changes nuclear coordinates). The former establishes an almost monotonic decrease of fluorescence by transferring energy from excitons to phonons. The latter happens because electronic transition dipole moments depend on the nuclear coordinates, as dictated by Herzberg-Teller theory. Recently, Herzberg-Teller selection rules were found to be essential to describe vibronic coupling in stacked perylenetetracarboxylic acid diimides either in intermolecular or in intramolecular interactions.[8] It was demonstrated that intermolecular electronic coupling within the stacks results in multiple low-energy electronically excited states that all contribute to the optical spectrum.[8]

In this work, PL measurements are made on a $K_4PTC$ film and its PL dependency on temperature is investigated. For comparison, fluorescence of the molecule is measured in aqueous solution. Among the spectral features, there are some which are easily identified, associated to Frenkel excitons, that slowly quenches, with rising temperature, in an intermediate temperature range (from 50 to 150 K). However, in the high temperature range, up to 300 K, there are some which are thermally activated and regain intensity. Previous findings on $Tb(H_3PTC)_3$ are compared and a similar behavior indicates that, in the high temperature range, Herzberg-Teller (HT) selection rules must be applied in order to explain the phenomena. In this work, we show, through temperature investigation of luminescence properties, that molecules with no internal rotational degrees of freedom show aggregation induced luminescence enhancement (AIE) at room temperature. Particularly, one of these molecules, $K_4PTC$, shows a series of spectral features in which the light emission energy range lies within the bound exciton fundamental energy.

## 2. Experimental details

### 2.1. Synthesis of $K_4PTC$

The preparation of $K_4PTC$ is described in detail by Wang et. al. in ref.[7]

Briefly, 3.363 g of potassium hydroxide at 85% concentration was diluted in 30 ml of deionized water, followed by the addition of 3.937 g of PTCDA and 10 ml of water. The solution was stirred for a day with a magnetic stirrer and then dumped into a beaker containing 300 ml of ethanol, in which a yellow precipitate was immediately formed. The mixture was then dried under vacuum, resulting in a yellow powder, highly soluble in water and with intense fluorescence.

### 2.2. Photoluminescence measurements

#### 2.2.1. PL of bulk $K_4PTC$ samples

Photoluminescence emission was measured using a closed loop helium cryostat, spanning from a temperature of 10 K to 300 K using the 454 nm line of a solid state laser. Quantamaster spectrometer from PTI-Horiba-JobinYvon equipped with a Photomultiplier Hamamatsu R928S for the visible range up to 900 nm was used. Time-decay measurements were done with a NanoLed ($\lambda_{exc}$ = 454 nm) at T = 300 K at different wavelengths.

#### 2.2.2. PL of $K_4PTC$ and $Tb(H_3PTC)_3$ in aqueous solutions

Photoluminescence emission in aqueous solutions was measured using a Varian Carry Eclipse spectrophotometer from Agilent, with a mirrored cuvette (double pass).

#### 2.2.3. PL Quantum yield of in bulk and solutions of $K_4PTC$ and $Tb(H_3PTC)_3$

The emission quantum yields (QY) of the solutions and bulk samples were measured by the integrating sphere (Ocean Optics) method. ($\lambda_{exc}$ = 371 nm)

### 2.3. X-ray powder diffraction

X-ray diffraction (XRD) measurements were carried out for PTCDA and $K_4PTC$ for dry (powder) samples using Cu-Kα radiation from a Panalytical Empyrean diffractometer.

## 3. Results and Discussion

The evolution of PL signal with temperature is shown in Fig.2.

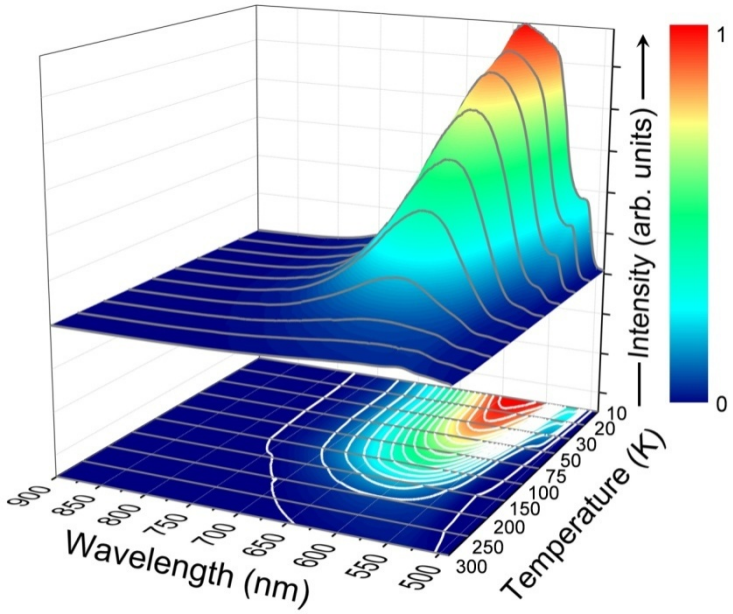


Fig. 2.Temperature-dependent PL spectra of $K_4PTC$.

The emission of $K_4PTC$ is depicted along the temperature range used in this work in figure 2. A clear intensity reduction is observed for all peaks as temperature increases. This is similar to what happens with $Tb(H_3PTC)_3$, as reported in ref.[3] . Nevertheless, a closer look reveals that each peak presents a particularly distinct temperature dependency behavior. Such result implies on the coexistence of distinct recombination processes, each one taking place at a different temperature range, associated with the stability of the process itself, as well as with the influence of vibrational modes on each observed emission channel.

Previous studies on PTCDA show the existence of several light-emitting interactions, which are identified through PL and its temperature dependency.[9] The most intense peak is observed at lower temperatures (2.03 eV) as shown in Fig. 3. This peak might be associated to Frenkel exciton recombination.[10] Therefore, other processes should be considered to explain the position of the other peaks in the spectra. Gaussian function fittings of the data represented in Fig. 2 are shown in Fig. 3, allowing the establishment

between the intensity of each of the phenomena and the system temperature. Such analysis allows us to identify the most intense band (Frenkel exciton) and the other (CT or excited exciton states of Frenkel exciton, most probably the latter) at 2.18, 2.30, 2.42 and 2.51 eV. The integrated intensity (peak area) of each process is depicted as a function of temperature in Fig. 4 and the peak intensity of each process as a function of temperature in the SI (Fig. S1).

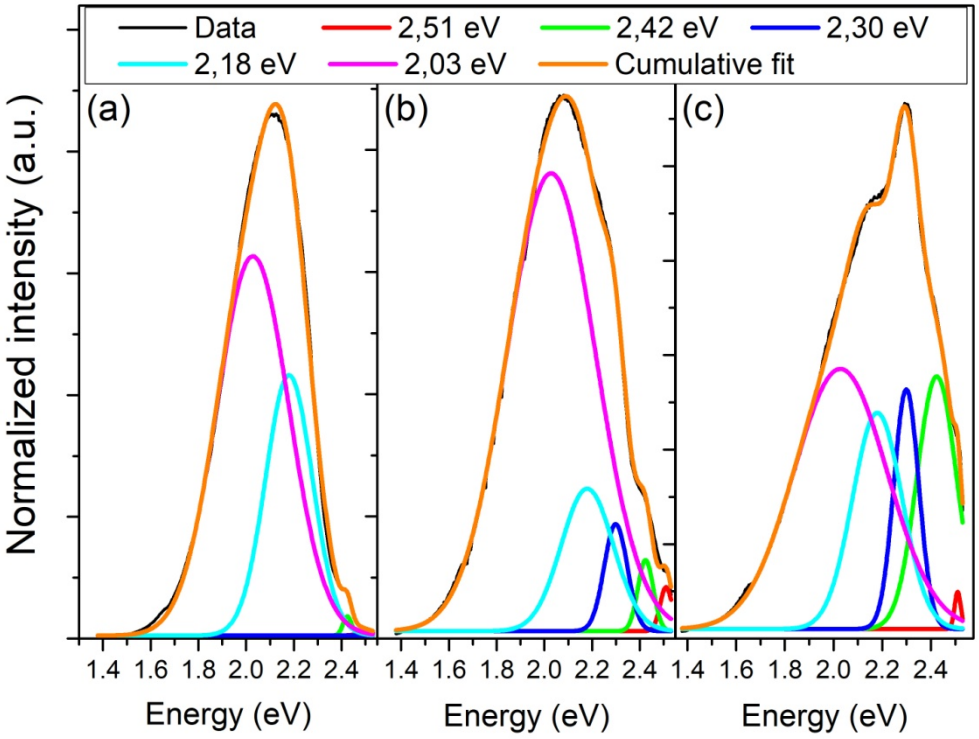


Fig. 3. Gaussian fitting functions of the PL signal. Photoluminescence measurements at different temperatures, at (a) 50 K, (b) 200 K and (c) 300 K, and gaussian-fit-peaks for each exciton process.

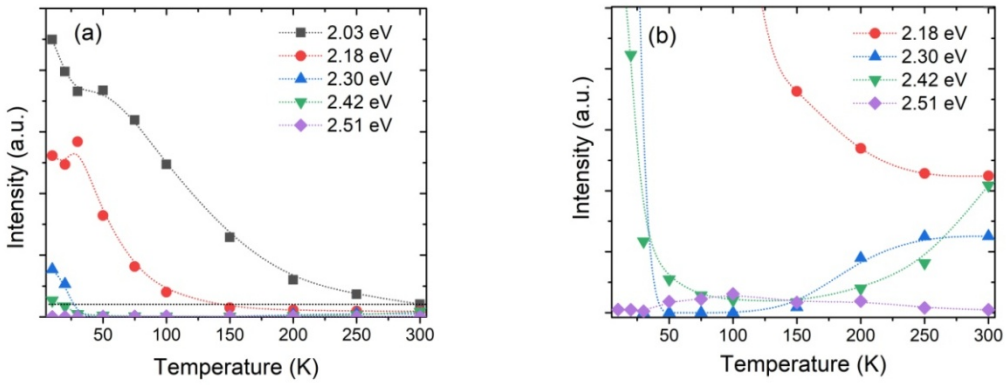

Fig. 4. a) Temperature dependence of each luminescence process (integrated area). b) y-scale expanded view of graphic (a).The horizontal dotted line in (a) corresponds to the upper limit in (b). Dotted lines serve as a guide to the eyes solely.

However, there is an outstanding difference between PTCDA and $Tb(H_3PTC)_3$,[3] or PTCDA and $K_4PTC$ which is more pronounced in the latter case. In the high temperature range, up to 300 K, some peaks regain intensity, after almost vanishing in the intermediate temperature range. These phenomena are not observed in PTCDA, according to the literature.[10] Since every peak is related to an allowed electronic transition, the peaks that appear in the higher temperature range are excitonic recombinations that have passed from a forbidden condition to an allowed one. This can only happen through vibronic coupling via Herzberg-Teller (HT) selection rules.

PTCA, the acid form of PTCDA, had already shown HT selection rules in charge transfer resonances in surface-enhanced Raman scattering.[11] In that work, Ma et al. observed an enhancement of vibrational modes at specific energy excitations. In that particular case, the presence of a metal interface was considered to explain the spectra.[11]

However, organic aggregates can present an aggregation-enhanced emission from an excited dark state in solid phase.[12] According to Yin et al., vibronic coupling or the Herzberg–Teller (HT) effect,[13] an interaction between electronic and nuclear motion, is a phenomenon through which additional radiative intensity is provided from intermediate allowed states via certain normal modes,[13] resulting on the appearance of luminescence from a "dark" state, under particular conditions.[12] They also state that the HT effect in the solid-state luminescence has been rarely considered and the influence of aggregation on the vibronic transition has been scarcely investigated.[12] In fact, there are few studies about aggregation-induced emission in the solid phase at low temperature.[11,14-16]

Understanding the dependency of aggregation-induced emission (AIE) in these perylene derivatives with temperature is noteworthy since the performance of future OLED devices with such perylene derivatives as moieties (i.e., grafted to already known compounds which show thermally-assisted delayed fluorescence) may be affected by the phenomenon.[17-19]

Aside the temperature dependency, evidence of AIE in bulk $K_4PTC$ is found when comparing PL (or fluorescent emission) with the molecule in aqueous solution. Fig. 5 shows the spectra of $K_4PTC$ in solution and bulk. For comparison, $Tb(H_3PTC)_3$ (bulk) and in aqueous solution is also shown. The spectra of the different products of PTCDA in solution are strikingly similar. And, although $K_4PTC$ spectra, both in solid and solution form, have emission peaks in the same range, a peak at 2.3 eV (539 nm) is present in the solid form. According to ref.[3], bulk emission of $Tb(H_3PTC)_3$ depends on the film thickness. These results point out to aggregation as the main responsible for the appearance of such peak.

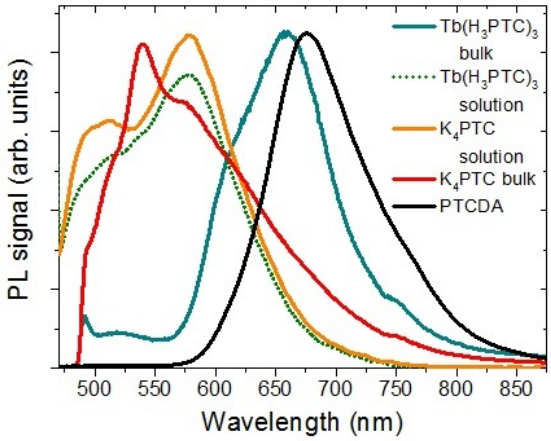


Fig. 5 Comparison between PL signal of $K_4PTC$ bulk (red), $K_4PTC$ in aqueous solution (orange) and $Tb(H_3PTC)_3$ bulk (green) and in aqueous solution (green dotted line). PL of PTCDA bulk is also shown (black). Measurements were carried out at T = 300 K.

Additional information on light emission processes is provided by time-dependent PL measurements (Fig. S2 and S3, in the supplementary information, SI) and concisely shown in Fig. 6. where the decay time is measured for different wavelengths in bulk (510 nm, 545 nm and 580 nm) and in solution (482 nm, 515 nm and 550 nm) corresponding to each process at T= 300 K. The slowest processes in $K_4PTC$ bulk have a lifetime of tens of ns (fig. 6a). In our previous work, we have found that exciton processes on $Tb(H_3PTC)_3$ bulk are also of tens of ns. When in solution, however, the lifetime is just a few ns, for both $K_4PTC$ and $Tb(H_3PTC)_3$. This is similar to what was found for 5,10 - diphenylphenazine in ref.[12], a molecule which AIE is associated to HT effect. However, in that work, the solid form of that molecule was crystalline and it has internal rotational degrees of freedom, which are absent in $K_4PTC$.

In a previous work by Kathiravan et al, a biexponential behavior of the time decay of the fluorescence of a pyrene derivative (4-((Pyren-1-ylmethylene)-amino)phenol) was associated to photoinduced charge transfer.[20] The mechanism of AIE of that molecule was determined as a suppression of photoinduced charge transfer (PCT) due to hydrogen bonding interaction of the imine donor of the molecule with water.[20] The smallest of the lifetimes would be the result of a quenching of the pyrene moiety by the imine group, while the other would be the unquenched decay of the molecule.[20] Since $Tb(H_3PTC)_3$ has several carboxylic groups, hydrogen bond formation during solvation could also happen and that would explain the biexponential behavior in our previous work, for the solid form of this complex.[3] $K_4PTC$, in aqueous solution, could in principle show a similar mechanism, regarding the carboxylate group. Particularly for $K_4PTC$, this would be the underlying reason for AIE since this molecule has no internal rotational degrees of freedom. Therefore, AIE for both molecules, can be explained by the same mechanism.

We also measured the quantum yield (QY) for the molecules. The features of AIE emission in bulk have a QY of 1.2% for $K_4PTC$ and of 30% for $Tb(H_3PTC)_3$. Following solubilization, the same features have a QY of 0.36% for $K_4PTC$ and of 25% for $Tb(H_3PTC)_3$.

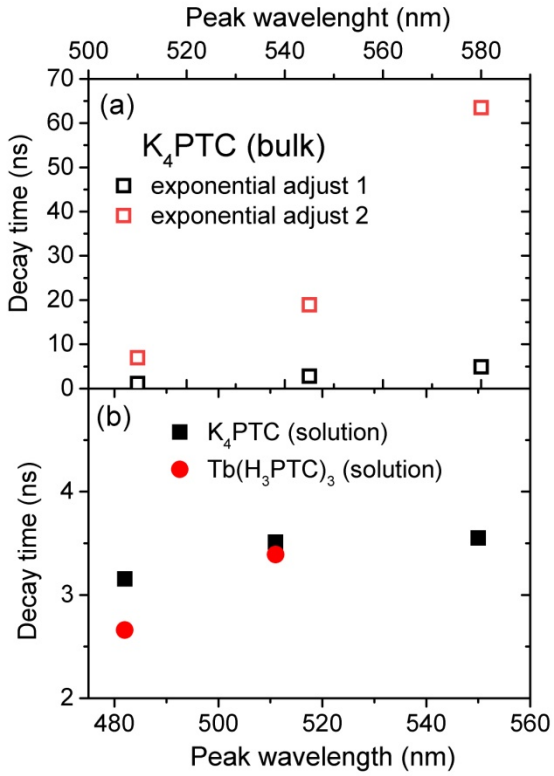


Fig. 6. a) Lifetime of the processes present in the PL emission of $K_4PTC$ (bulk) fitted with bi-exponential decays. b) lifetime of the processes present in the PL emission of $K_4PTC$ and $Tb(H_3PTC)_3$ in solution fitted by exponential decays. The PL-decay measurements of different exciton components fitted are provided in the supplementary information, in fig. S2 and S3 (SI). Measurements were carried out at T = 300 K.

The reason for the absence of the AIE in PTCDA is more evident. Usually, PTCDA aggregation results at π- stacking, which allows electron delocalization inside the stack, what can be devised through excimer emission.[9] This is a more probable de-excitation pathway, once the molecular stack is formed.[21-29]

$Tb(H_3PTC)_3$ molecules cannot be easily stacked, due to its three-fold geometry,[3] and that should happen as well to $K_4PTC$, due to the potassium atoms large radii, which would prevent long-range π-stacking.[7]

Fig. 7 shows that XRD results for PTCDA are similar to previous measurements on β-phase powders reported in refs [29, 30]. XRD measurements performed on $K_4PTC$ along the same diffraction range and with same integration time show less pronounced and broader peaks (see fig.7 inset), indicating that $K_4PTC$ exhibits a lower degree of long-range order and presents smaller crystalline domains. Even though different from PTCDA, such result on a dry $K_4PTC$ specimen resembles the pattern for stronger peaks

observed in PTCDA α phase.[30] Such difference in molecular aggregation may also impact on $K_4PTC$ emission in solution.

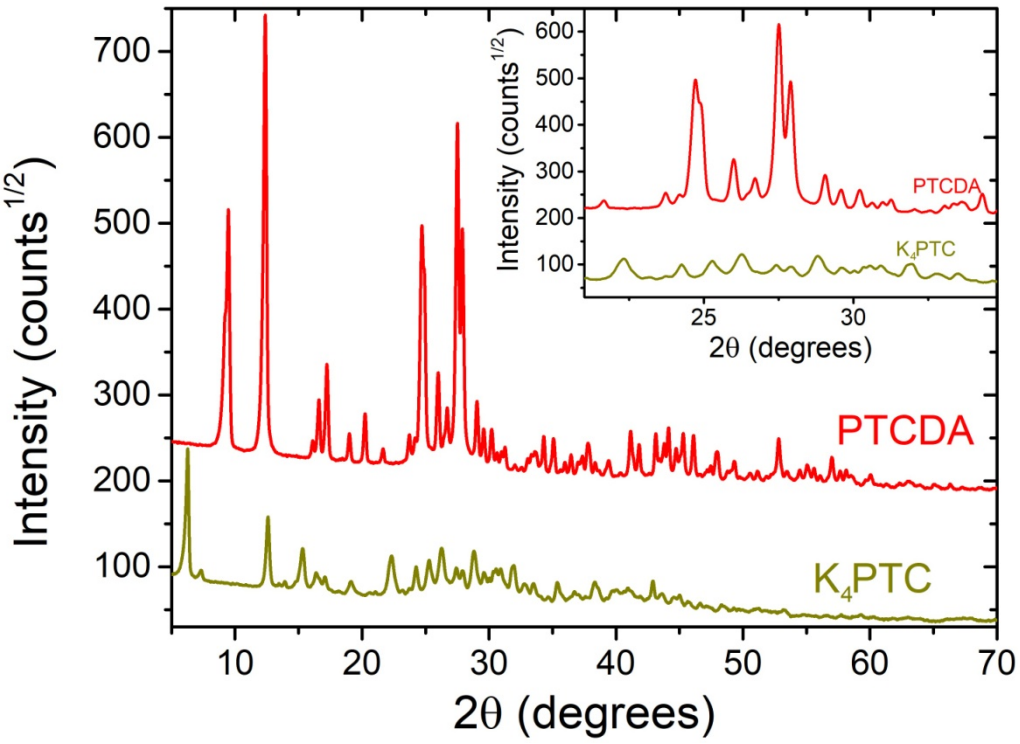


Fig. 7. X-ray diffraction data measured for dry PTCDA and $K_4PTC$ samples using a standard Cu-Kα source (λ = 0.154 nm). Similar sample volumes were measured for the same integration time (curves are displaced for clarity by adding a fixed constant value to PTCDA points). The inset depicts a limited interval for both curves between 21° and 39° in scattering angle, indicating the reduced $K_4PTC$ crystallinity and smaller domain size (larger diffraction peaks).

At least in the high temperature range, i. e., above 100 K, the phonon thermal bath is capable to enhance emission peaks in both $Tb(H_3PTC)_3$ and $K_4PTC$. The same energies of that peaks are found in the lowest temperature range in $Tb(H_3PTC)_3$. For both molecules, some peaks almost vanish at T~ 50 K and reappear at 150 K.

We suggest that the observed energies, for bulk samples, are from excited exciton states in the whole temperature range, aside from the fundamental states of the bound excitons, in both molecules. In $K_4PTC$, the intensities follow a clear picture. At low temperatures, the exciton fundamental states, are the most probable to appear. As the temperature rises, phonon scattering diminishes their intensity, to some cases, almost vanishing. Nevertheless, further increase in temperature causes vibronic coupling to enhance the emission of some peaks, specially the more excited exciton bound states. In such cases, transitions that are forbidden under Franck-Condon rules become allowed under Herzberg-Teller rules. The bound exciton fundamental energy theoretically

expected for $K_4$PTC corroborates this picture,[3, 32] since its value is around the same energy difference between the Frenkel exciton fundamental energy (2.03 eV) and the emission energy of the highest energy peak. In fact, the lifetime measured at 539 nm is the shortest of the series measured at room temperature for $K_4$PTC bulk (fig. 6). The order of the slowest process of the bi-exponential decays of each process at room temperature indicates that the more energetic transitions are faster. That corroborates our previous suggestion that the observed energies are excited (and fundamental) exciton states of the bound excitons.

Further studies are necessary, to fully understand the PL mechanisms, or if the molecule could show mechanochromism, for instance.[33]

## 4.Conclusion

Temperature dependent photoluminescent properties of $K_4$PTC, a perylene derivative have been investigated in the solid and aqueous solution of the molecule, show aggregation-induced enhanced PL-emission at room temperature. The different excitonic processes are dependent of temperature, some of which are only present above 150 K. Herzberg-Teller selection rules enable exciton excited states to turn from "dark" to "bright" states, the most probable reason to this phenomenon. $K_4$PTC, a molecule comparable to the size of PTCDA, is highly soluble in water, contrary to PTCDA, which is poorly soluble in most of solvents. The molecule could, in principle, be used as a biomarker, or in photodynamic therapy, if further studies show relatively low toxicity.

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## Author Contributions

All the authors made substantial contribution while preparing the manuscript.

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## Data Availability

Authors can confirm that all relevant data are included in the article and/or its supplementary information files.

## Code Availability

Not applicable.

## Author Declarations

## Conflicts of interest

The authors declare that there is no conflict of interest.

## Ethical Approval

This article does not contain any studies with human or animal subjects.

## Informed Consent

A statement regarding informed consent is not applicable.

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